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(54) Title of the invention

Method for forming an amorphous organic film

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SPECIFICATION

1. Title of the invention

Method for forming an amorphous organic film

2. Claims

1. A method for forming an amorphous organic film, which is a method for forming a thin film by vapor deposition characterized in that the organic material is exposed to light as it is vapor-deposited in order to obtain a film.
2. A method for forming an amorphous organic film as described in Claim 1, characterized in that said exposure to light is accomplished by exposing the organic material to light in the gaseous state during vapor deposition.
3. A method for forming an amorphous organic film as described in Claim 1, characterized in that said exposure to light is accomplished by exposing the film to light as it is laid down.
4. A method for forming an amorphous organic film as described in Claim 1, characterized in that said exposure to light is accomplished by exposing both the organic film being laid down and the organic

material in the gaseous state to light during vapor deposition.

5. A method for forming an amorphous organic film as described in Claim 1, characterized in that said exposure to light is accomplished by exposing the organic material to light on the heating boat during vapor deposition.

6. A method for forming an amorphous organic film as described in any one of Claims 1-5, characterized in that, when several organic materials are deposited simultaneously during said vapor deposition, vapor deposition is performed by exposing at least one of the organic materials to light..

7. A method for forming an amorphous organic film as described in Claim 1, characterized in that a spiropyran, stilbene, azobenzene or fulgide organic material which undergoes a structural change on exposure to light is used as said organic material.

3. Detailed description of the invention

[Field of industrial application]

The present invention relates to a method for forming thin films using organic materials which, on exposure to light, absorb light and change color, molecular structure, crystal structure, electronic state, bonding state or polarity, etc., so that vapor deposition films thereof become glassy amorphous thin films.

[Prior art]

Organic thin films can be formed by various methods, such as sputtering, vapor deposition, spin coating, dipping or Langmuir-Blodgett techniques.

Of these, vapor deposition is a dry process which enables the formation of thin films without using a solvent or dispersant or any other material, and therefore it is easy to control film thickness, and it can be used to form multilayer thin films and mixed thin films with organic materials in any proportions.

Moreover, vapor deposition is inevitably accompanied by a process of purification by sublimation, so that it is possible to obtain thin films from pure substances without impurities.

However, it involves heating in a vacuum at the vicinity of the boiling point or sublimation point, and this can cause thermolysis of organic materials. In addition, many types of organic materials only give an opaque microcrystal-containing or polycrystalline organic thin film when the film is formed by vacuum-vapor deposition. In other cases an organic material may give a glassy amorphous thin film in a vacuum, but this crystallizes in air and becomes cloudy and opaque.

Organic materials which show photochromism due to a molecular change on exposure to light, such as spiropyrans, and fulgides (general term for bis-methylenesuccinic anhydrides) for example, and organic compounds typically showing a *cis/trans* isomeric switch, such as azobenzenes and stilbenes for example, nearly

all form opaque microcrystalline thin films on vapor deposition, and as indicated above, it is difficult to form glassy amorphous thin films by any method for forming a thin film.

[Problem which the invention is intended to solve]

The present invention offers a vapor deposition method which makes it possible to form glassy amorphous thin films even with organic materials which do not give glassy amorphous thin films with prior techniques for forming organic thin films from organic materials by using vapor deposition because of crystallization, oxidation or decomposition.

[Means for solving the problem]

To explain the present invention, the present invention relates to a method for forming amorphous organic films by vapor deposition, characterized in that the vapor deposition is carried out while exposing the organic material to light.

The principal feature of the present invention is that an organic material which absorbs light when it is exposed to light, and undergoes a change in color, molecular structure, crystal structure, electronic state, bonding state or polarity, etc., is exposed to light as it is formed into a thin film by vapor deposition, to give a glassy amorphous thin film.

With prior vapor deposition methods, nearly all organic materials become cloudy due to crystallization, etc. However, by using the present invention it is possible to obtain glass amorphous organic thin films

which cannot be obtained by prior techniques, without changes in crystal structure, because said organic material absorbs the light to which it is exposed and undergoes a change in color, molecular structure, crystal structure, electronic state, bonding state or polarity, etc.

Moreover, by forming said compound into an amorphous thin film, free voids are formed around the molecules of said compound in the amorphous thin film which are not present in the crystal structure.

In the case of spiropyrans, this facilitates the change in the molecular structure associated with photochromism, and photochromic efficiency is greatly increased compared with crystalline thin films. The quantum absorption rate of stilbenes and azobenzenes, which are typical of compounds which show a change in molecular structure with a *cis/trans* isomeric change on exposure to light, is also greatly increased in amorphous thin films compared with crystalline thin films.

Similarly, the quantum absorption rate of fulgides, which are typical of compounds which undergo (E) \rightleftharpoons (Z) isomerism as a result of molecular movement due to exposure to light, is also considerably increased in amorphous thin films compared with crystalline films.

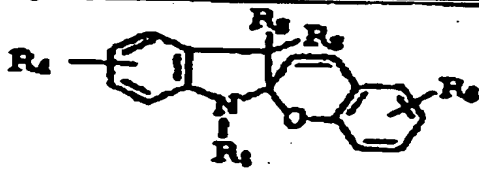
The exposure of the organic material to light can be performed with the organic material in any state during the vapor deposition process. It can be performed, for example, on the organic material in the

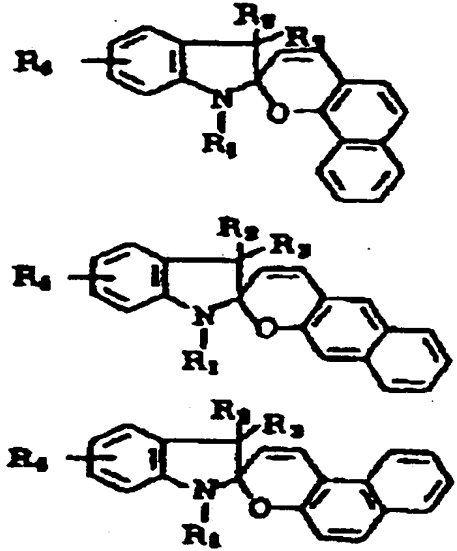
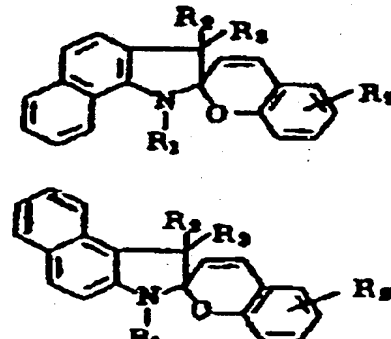
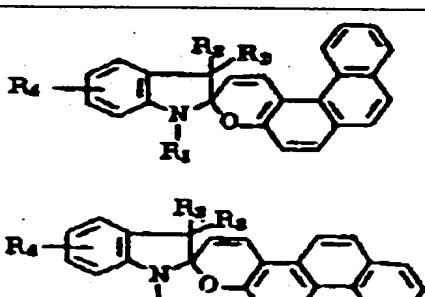
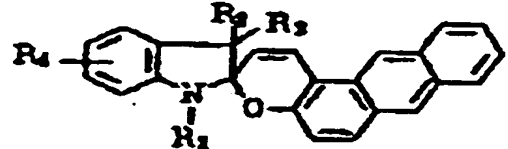
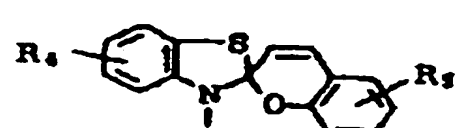
gaseous state, on the organic material on the heating boat during vapor deposition, or on the organic material forming a thin film on the substrate. The exposure to light can also be exposure of the organic material to light through the substrate when a transparent substrate is used. When several different organic materials are vapor-deposited at the same time by the method of the present invention, vapor deposition can be performed with only one of the organic materials being exposed to light.

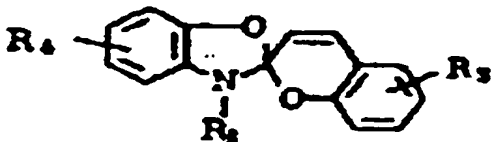
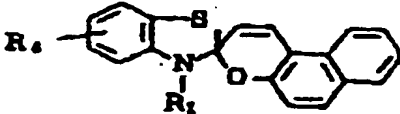
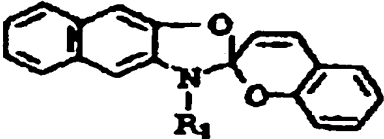
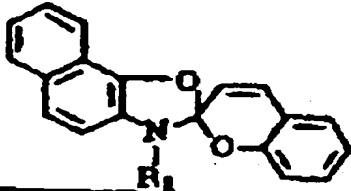
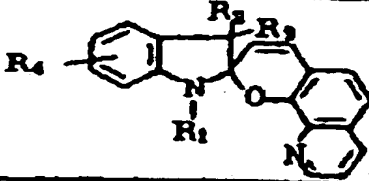
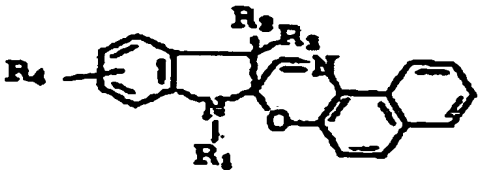
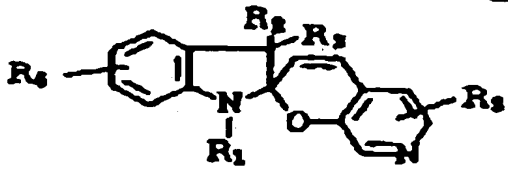
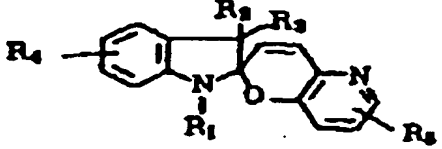
The light used in the present invention is not restricted to visible light, but with high energy radiation there is a danger that the organic materials will decompose, and therefore it is generally desirable to use a source of light in the region from ultraviolet to infrared.

Spiropyrans, fulgides, stilbene and azobenzenes can be cited as compounds which undergo a change in color, molecular structure, crystal structure, electronic state, bonding state or polarity, etc.

Table 1 presents the names and basic structural formulae of some spiropyrans.

Table 1	
Compound	Basic structural formula
Spiro[2H-1-benzopyran-2,2-indoline]	 <p>The diagram shows the chemical structure of a spiro compound. It consists of a benzopyran ring system (a benzene ring fused to a pyran ring) and an indoline ring system (a benzene ring fused to a pyrrolidine ring). The two ring systems are connected at their 2-positions by a spiro carbon atom. This central carbon atom is also bonded to two other groups, labeled R2 and R3. The indoline ring has a nitrogen atom at the 1-position, which is bonded to a group labeled R4. The benzopyran ring has a substituent R1 at the 3-position and another substituent R5 at the 4-position. The pyran ring has an oxygen atom at the 1-position.</p>

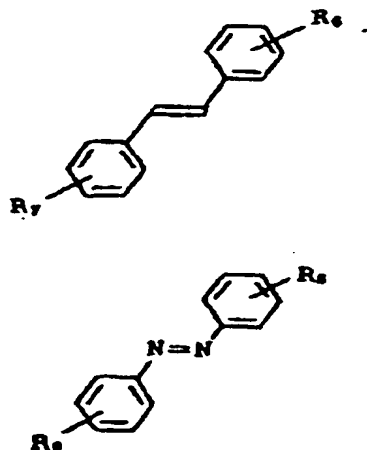
Spiroindolinonaphthopyran	
Spirobenzoindolino- benzopyran	
Spiroindolinophenanthrolo- pyran	
Spiroindolinoanthrapyran	
Spiro[2H-1-benzopyran-2,2'- benzothiazoline]	

Spiro[2 <i>H</i> -1-benzopyran-2,2'-benzoxazoline]	
Spiro[benzothiazoline-2,3'-[3 <i>H</i>]-naphtho[2,1- <i>b</i>]pyran]	
Spiro[2 <i>H</i> -1-benzopyran-2,2'-naphtho[2,3- <i>d</i>]oxazoline]	
Spiro[2 <i>H</i> -1-benzopyran-2,2'-naphtho[2,1- <i>d</i>]oxazoline]	
Spiro[benzopyran-2,2'-pyran[3,2- <i>H</i>]quinoline]	
Spiro[indoline-2,3'-[3 <i>H</i>]-naphtho[2,1- <i>b</i>]-1,4-oxazine]	
Spiro[indoline-2,2'-2[<i>H</i>]-pyrano[3,4- <i>b</i>]pyridine]	
Spiro[indoline-2,2'-[2 <i>H</i>]-pyrano[3,2- <i>b</i>]pyridine]	

Spiro[indoline-2,2'-[2H]-pyrano[3,2-c]quinoline]	
Spiro[2H-1,4-benzoxazine-2,2'-indoline]	
Spiro[2H-1-benzopyran-2,2'-[2H]quinoline]	
Spiro[3H-naphtho[2,1-b]pyran-3,2'-[2H]quinoline]	
Spiro[2H-1-benzopyran-2,2'-[2H]pyridine]	
Spiro[3H-naphtho[2,1-b]pyran-3,2'-[2H]pyridine]	

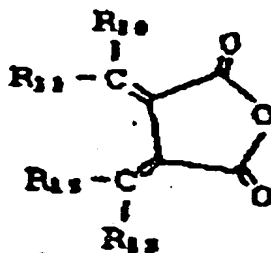
In the formulae, R_1 - R_3 , which can be the same or different, can be hydrogen or a lower alkyl group; R_4 and R_5 , which can be the same or different, are hydrogen, a lower alkyl group, a lower alkoxy group, nitro group, hydroxyl group or halogen.

Stilbenes and azobenzenes include organic compounds with one of the basic structures shown below.



(In the formula above, R₆-R₉, which can be the same or different, are hydrogen, lower alkyl group, lower alkoxy group, nitro group, hydroxyl group, halogen, amino group, or a mono- or di-substituted amine group.)

Fulgides include compounds with the basic structural formula.



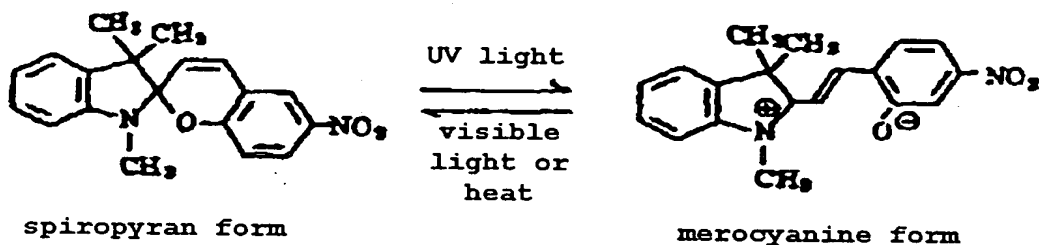
(In the formula, R₁₀-R₁₃, which can be the same or different, can be hydrogen or a substituent group; however, at least one is a group having an aromatic ring).

[Embodiments]

The present invention is described more specifically below by means of practical embodiments; however, the present invention is not restricted to these embodiments.

Embodiment 1

Fig. 1 is a schematic cross-sectional drawing of the device used in Embodiment 1 for forming an amorphous organic thin film. In Fig. 1, 11 is a bell jar, 12 is the substrate, 13 is ultraviolet light; 14 is an ultrahigh pressure mercury lamp, 15 is a slit, 16 is the sample material, 17 is a heating boat, 18 is a heating temperature control device, 19 is a quartz glass window, and 20 is a colored glass filter. The organic material used was 1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline] (code: NBPS), which undergoes a structural change on exposure to UV light. The structural change involved is shown by the equation below.



The heating boat 17 in Fig. 1 was heated to 170°C by the heating control device 18 in Fig. 1, and vapor deposition was carried out at a vacuum of 1×10^{-4} Torr,

with the NBPS being exposed in the gaseous state to ultraviolet light at 360 nm, using a 500 W ultrahigh pressure mercury lamp as the light source. On exposure to UV light, NBPS undergoes a change in molecular structure from the spiropyran form to the merocyanine form as indicated in the aforementioned equation. When NBPS is vapor-deposited by conventional vacuum-vapor deposition it gives only an opaque thin film, due to crystallization. However, when vapor-deposited while exposed to UV light by the present invention using a structure such as that illustrated in Fig. 1, the molecular structure of the NBPS undergoes a change from the spiropyran form to the merocyanine form, and the conversion to the counterion form is accompanied by a change in polarity, which prevents crystallization, and as a result it gives a glassy amorphous organic thin film.

Fig. 2 shows the results of studies on the surface roughness of a NBPS thin film formed by conventional vapor deposition and a NBPS thin film obtained by the present invention by a surface roughness meter, in the form of spectral diagrams. Fig. 2-1 is the surface of a NBPS thin film obtained by the prior method and Fig. 2-2 is the surface of an NBPS thin film obtained by the method of the present invention. It is evident that the surface of the NBPS thin film obtained by the method of the present invention is smooth and free of undulations because there are no crystals present. Similarly, Fig. 3 shows absorption spectra (x-axis, wavelength (nm); y-

axis, absorbance) of an NBPS thin film obtained by the prior method (broken line a) and the NBPS thin film obtained by the method of the present invention (solid line b). In both cases, the substrate was transparent quartz glass. The NBPS thin film obtained by the prior method was cloudy and opaque, due to crystallization, and consequently increased absorbance was observed over the entire measurement wavelength range due to light scattering. The NBPS thin film obtained by the method of the present invention showed no absorbance outside the region of absorption due to the merocyanine form, and was entirely transparent. Moreover, the absorption due to the merocyanine form was decreased by heating or exposure to visible light due to reversion to the spiropyran form, which is colorless in the visible light range, so that it was possible to obtain a colorless transparent glassy NBPS vapor deposition film, shown by the solid line c in Fig. 3. This film became colored when exposed again to UV light, and it was thus possible to obtain an amorphous NBPS film which showed photochromism in the amorphous state.

Fig. 4 presents graph showing the relationship of wave number (cm^{-1} , x axis) and relative intensity (y-axis) in the infrared (IR) absorption spectra of the NBPS thin film obtained by conventional vacuum-vapor deposition and the NBPS thin film obtained by the method of the present invention. Fig. 4-1 is the IR spectrum of the NBPS thin film obtained by the prior method, and Fig. 4-2 is the IR spectrum of the NBPS film obtained by

the method of the present invention. Fig. 4-1 shows absorption due to the spiropyran form, 690 cm^{-1} , (bending, *cis*-CH=CH-), 820 cm^{-1} (CH angle change, tri-substituted alkene, >CH=CH-), 1280 cm^{-1} (C-O-C asymmetric stretching, cyclic ether), 1340 cm^{-1} (>N-CH₃) and 1658 cm^{-1} (C=C stretching, *cis*-CH=CH-). By contrast, in the IR spectrum of Fig. 4-2, absorption appears at 1690 cm^{-1} (C=C stretching, *trans*-CH=CH-) due to the merocyanine form, but the other absorbance above due to the spiropyran form are absent. From this it is evident that the NBPS thin film formed by the method of the present invention is a thin film of the merocyanine form laid down as it stands on the substrate, which is impossible by the prior method. The merocyanine form of NBPS is an intramolecular zwitterion, and therefore molecular interaction during vapor deposition differs from the spiropyran form, and it is evident from the IR spectrum that, principally due to the effects of the increase in polarity, crystallization does not take place and an amorphous organic film is obtained.

Embodiment 2

Fig. 5 is a schematic cross-sectional drawing of the device employed in Embodiment 2 for vapor deposition of an amorphous organic thin film. In Fig. 5, 51 is a 500 W ultrahigh-pressure mercury lamp, 52 is a reflecting mirror, 53 is a glass bell jar transparent to UV light at 365 nm, 54 is a quartz glass substrate, 55 is the sample material 56 is a heating boat, 57 is a heating temperature control device, 58 is the light beam

and 59 is a colored glass filter. A transparent quartz plate was used as the substrate and this was lit from behind so that the sample material was exposed to light in the gas phase during vapor deposition as the thin film was laid down on the substrate, and on the heating boat. The sample material used was NBPS as in Embodiment 1 and other conditions were also the same as in Embodiment 1. By carrying out vapor deposition on a transparent substrate while exposing it to light in this way, it was also possible to obtain the transparent glassy amorphous thin film of NBPS obtained in Embodiment 1, and the properties thereof were also as in Embodiment 1.

Embodiment 3

Fig 6 is a schematic cross-sectional drawing of the device employed in Embodiment 3 for vapor deposition of an amorphous organic thin film. In Fig. 6, 61 is a 500 W ultrahigh-pressure mercury lamp, 62 is a reflecting mirror, 63 is a glass bell jar transparent to UV light at 365 nm, 64 is a silicon (Si) substrate, 65 is the sample material, 66 is a heating boat, 67 is a heating temperature control device, 68 is the light beam and 69 is a colored glass filter. In this case an opaque Si substrate was used, and therefore the thin film was exposed to light as it was laid down on the substrate by illumination from the front of the substrate. The sample material used for vapor deposition was NBPS as in Embodiment 1, and the other conditions were also the same as in Embodiment 1. By using an opaque substrate

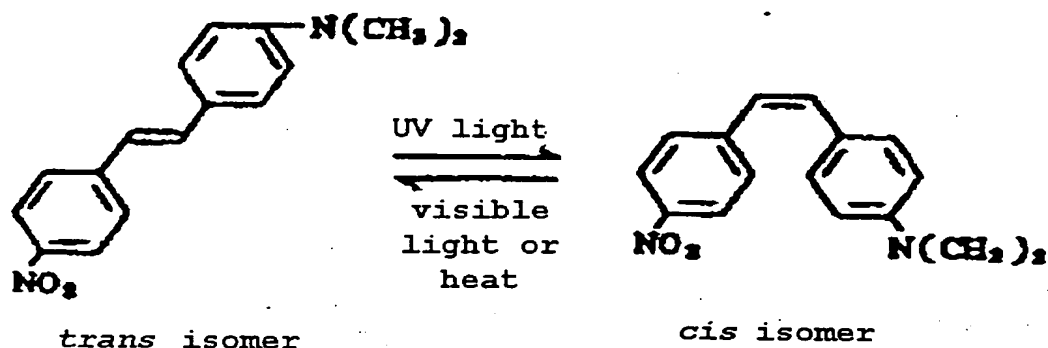
and carrying out vapor deposition while exposing the substrate to light in this way it was also possible to obtain the transparent glassy amorphous thin film of NBPS obtained in Embodiment 1, and the properties thereof were also the same as in Embodiment 1.

Embodiment 4

Fig 7 is a schematic cross-sectional drawing of the device employed in Embodiment 4 for vapor deposition of an amorphous organic thin film. In Fig. 7, 71 is a 500 W ultrahigh-pressure mercury lamp, 73 is a glass bell jar transparent to UV light at 365 nm, 74 is the substrate, 75 is the sample material, 76 is a heating boat, 77 is a heating temperature control device, 78 is the light beam and 79 is a colored glass filter. The sample material used for vapor deposition was NBPS as in Embodiment 1, and the other conditions were also the same as in Embodiment 1. During vapor deposition, the solid NBPS on the heating boat is vaporized after melting and passing from the solid to the liquid state. In Embodiment 4, vacuum-vapor deposition was carried out under the same conditions as in Embodiment 1, while exposing the NBPS on the heating boat to UV light in this liquid state. By exposing the sample material on the heating boat directly to light in this way, it was also possible to obtain the transparent glassy amorphous thin film of NBPS obtained in Embodiment 1, and the properties thereof were also the same as in Embodiment 1.

Embodiment 5

The device illustrated in Fig. 1 was used. The organic sample material used was 4-nitro-4'-dimethylaminostilbene (abbreviation: NDASB), a compound which undergoes a *cis/trans* isomeric change. This structural change is represented by the equation below.



The heating boat 17 in Fig. 1 was heated to 80°C by the heating temperature control device 18 in Fig. 1, and vacuum-vapor deposition was performed at a vacuum of 1×10^{-4} Torr, with the NDASB being exposed in the gaseous state to ultraviolet light at 360 nm, using a 500 W ultrahigh pressure mercury lamp as the UV light source. When exposed to UV light NDASB undergoes a structural change by *cis/trans* isomerism indicated in the aforementioned equation. When NDASB is vacuum-deposited by conventional vacuum-vapor deposition, it only gives an opaque thin film due to crystallization. However, when vacuum-deposited by the method of the present invention, with exposure to UV light during vapor deposition by means of the structure of Fig. 1,

NDASB undergoes a structural change from *cis* to *trans*, which also alters the crystal structure thereof, and as a result it is possible to obtain a glassy amorphous thin film of NDASB.

Fig. 8 shows the absorption spectra (x-axis, wavelength (nm); y-axis, optical density (OD)) of thin films of NDASB obtained by the prior method (broken line a) and the method of the present invention (solid line b). In both cases the substrate used was a transparent quartz glass substrate. The NDASB film obtained by the prior method was cloudy and opaque, due to crystallization, and therefore showed increased optical density (OD) over the whole measurement wavelength range due to light scattering. By contrast, the NDASB thin film obtained by the method of the present invention showed no absorption except for the absorption due to the *cis* isomer, and was entirely transparent. Moreover, the absorption due to the *cis* isomer decreased on exposure to visible light, due to reversion of NDASB to the *trans* isomer, to give the glassy NDASB vapor deposition film indicated by solid line c in Fig. 8. When this film was again exposed to UV light it became colored, so that it was possible to obtain an amorphous NDASB thin film which showed a reversible *cis* / *trans* isomeric change in the amorphous state.

Embodiment 6

The device shown in Fig 5 was employed. The vapor deposition sample material used was NDASB as in Embodiment 5, and the other conditions were also the

same as in Embodiment 5. By direct exposure to light through a transparent substrate in this way it was also possible to obtain the transparent glassy amorphous thin film of NDASB obtained in Embodiment 5.

Embodiment 7

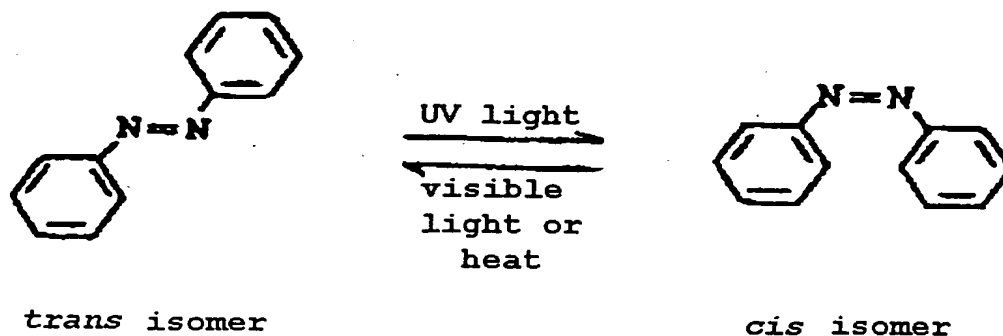
The device shown in Fig. 6 was employed. The vapor deposition sample material used was NDASB as in Embodiment 5, and the other conditions were also the same as in Embodiment 5. By using an opaque substrate and exposing to glass from the vapor deposition side in this way it was also possible to obtain the transparent glassy amorphous thin film of NDASB obtained in Embodiment 5.

Embodiment 8

The device shown in Fig. 7 was employed. The vapor deposition sample material used was NDASB as in Embodiment 5, and the other conditions were also the same as in Embodiment 5. During vapor deposition, the solid NDASB on the heating boat is vaporized after melting and passing from the solid to the liquid state. In Embodiment 8, vacuum-vapor deposition was carried out under the same conditions as in Embodiment 5, while exposing the NDASB on the heating boat to UV light in this liquid state. By exposing the sample material on the heating boat directly to light in this way it was also possible to obtain the transparent glassy amorphous thin film of NDASB obtained in Embodiment 5.

Embodiment 9

The device illustrated in Fig. 1 was used. The organic sample material used was azobenzene, a typical compound which undergoes a *cis/trans* isomeric change on exposure to UV light. The structural change is illustrated by the equation below.



The heating boat 17 in Fig. 1 was heated to 80°C by the heating temperature control device 18 in Fig. 1, and vacuum-vapor deposition was performed at a vacuum of 1×10^{-4} Torr, with the azobenzene being exposed in the gaseous state to ultraviolet light at 360 nm, using a 500 W ultrahigh pressure mercury lamp as the UV light source. As indicated in the aforementioned equation, when exposed to UV light azobenzene undergoes a structural change by *cis/trans* isomerism. When azobenzene is vacuum-deposited by conventional vacuum-vapor deposition, it only gives an opaque thin film due to crystallization.

However, when vacuum-deposited by the method of the present invention, with exposure to UV light during

vapor deposition by means of the structure of Fig. 1, azobenzene undergoes a structural change from *cis* to *trans*, which also alters the crystal structure thereof, and as a result it is possible to obtain a glassy amorphous thin film of azobenzene.

Fig. 9 shows the absorption spectra (x-axis, wavelength (nm); y-axis, optical density (OD)) of thin films of azobenzene obtained by the prior method (broken line a) and the method of the present invention (solid line b). In both cases the substrate used was a transparent quartz glass substrate.

The azobenzene film obtained by the prior method was cloudy and opaque, due to crystallization, and therefore showed increased optical density (OD) over the whole measurement wavelength range due to light scattering.

By contrast, the azobenzene thin film obtained by the method of the present invention showed no absorption except for the absorption due to the *cis* isomer, and was entirely transparent. Moreover, the absorption due to the *cis* isomer decreased on exposure to visible light, due to reversion of azobenzene to the *trans* isomer, to give the glassy azobenzene vapor deposition film indicated by solid line c in Fig. 9. When this film was again exposed to UV light it became colored, so that it was possible to obtain an amorphous azobenzene thin film which showed a reversible *cis* / *trans* isomeric change in the amorphous state.

Embodiment 10

The device shown in Fig 5 was employed. The vapor deposition sample material used was azobenzene as in Embodiment 9, and the other conditions were also the same as in Embodiment 9. By direct exposure to light through a transparent substrate in this way it was also possible to obtain the transparent glassy amorphous thin film of azobenzene obtained in Embodiment 9.

Embodiment 11

The device shown in Fig. 6 was employed. The vapor deposition sample material used was azobenzene as in Embodiment 9, and the other conditions were also the same as in Embodiment 9. By using an opaque substrate and exposing to glass from the vapor deposition side in this way it was also possible to obtain the transparent glassy amorphous thin film of azobenzene obtained in Embodiment 9.

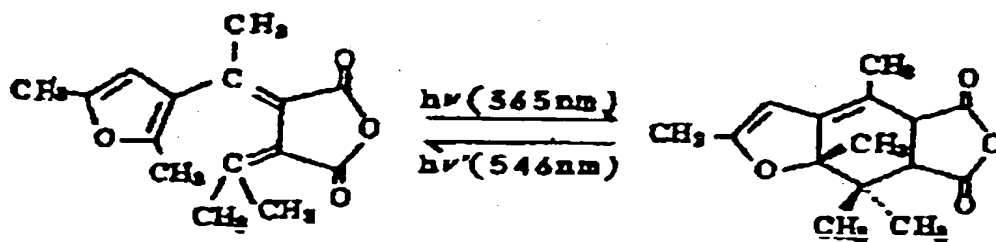
Embodiment 12

The device shown in Fig. 7 was employed. The vapor deposition sample material used was azobenzene as in Embodiment 9, and the other conditions were also the same as in Embodiment 9. During vapor deposition, the solid azobenzene on the heating boat is vaporized after melting and passing from the solid to the liquid state. In Embodiment 12, vacuum-vapor deposition was carried out under the same conditions as in Embodiment 9, while exposing the azobenzene on the heating boat to UV light in this liquid state. By exposing the sample material on the heating boat directly to light in this way it was

also possible to obtain the transparent glassy amorphous thin film of azobenzene obtained in Embodiment 9.

Embodiment 13

The device illustrated in Fig 1 was used. The organic sample material used was (E)- α -2,5-dimethyl-3-furylethylidene (7,7-dimethylmethylene)succinic anhydride (abbreviation: furylfulgide), which undergoes a structural change on exposure to UV light. The structural change is represented by the equation below.



The heating boat 17 in Fig. 1 was heated to 200°C by the heating temperature control device 18 in Fig. 1, and vacuum-vapor deposition was performed at a vacuum of 1×10^{-4} Torr, with the furylfulgide being exposed in the gaseous state to ultraviolet light at 360 nm, using a 500 W ultrahigh pressure mercury lamp as the UV light source. When exposed to UV light furylfulgide undergoes the structural change indicated in the aforementioned equation. When furylfulgide is vacuum-deposited by conventional vacuum-vapor deposition, it only gives an opaque thin film due to crystallization. However, when vacuum-deposited by the method of the present invention, with exposure to UV light during vapor deposition by

means of the structure of Fig. 1, furylfulgide undergoes a structural change, which also alters the crystal structure thereof, and as a result it is possible to obtain a glassy amorphous thin film of furylfulgide.

Fig. 10 shows the absorption spectra (x-axis, wavelength (nm); y-axis, optical density (OD)) of thin films of furylfulgide obtained by the prior method (broken line a) and the method of the present invention (solid line b). In both cases the substrate used was a transparent quartz glass substrate. The furylfulgide film obtained by the prior method was cloudy and opaque, due to crystallization, and therefore showed increased optical density (OD) over the whole measurement wavelength range due to light scattering.

By contrast, the furylfulgide thin film obtained by the method of the present invention showed no absorption except for the absorption due to the (Z) isomer, and was entirely transparent. Moreover, the absorption due to the (Z) isomer decreased on exposure to visible light, due to reversion of furylfulgide to the (E) isomer, to give the glassy furylfulgide vapor deposition film indicated by the solid line c in Fig. 10. When this film was again exposed to UV light it became colored, so that it was possible to obtain an amorphous furylfulgide thin film which showed a reversible (E) \rightleftharpoons (Z) change in the amorphous state.

Embodiment 14

The device shown in Fig 5 was employed. The vapor deposition sample material used was furylfulgide as in.

Embodiment 13, and the other conditions were also the same as in Embodiment 13. By direct exposure to light through a transparent substrate in this way it was also possible to obtain the transparent glassy amorphous thin film of furylfulgide obtained in Embodiment 13.

Embodiment 15

The device shown in Fig. 6 was employed. The vapor deposition sample material used was furylfulgide as in Embodiment 13, and the other conditions were also the same in Embodiment 13. By using an opaque substrate and exposing to glass from the vapor deposition side in this way it was also possible to obtain the transparent glassy amorphous thin film of furylfulgide obtained in Embodiment 13.

Embodiment 16

The device shown in Fig. 7 was employed. The vapor deposition sample material used was furylfulgide as in Embodiment 13. During vapor deposition, the solid furylfulgide on the heating boat is vaporized after melting and passing from the solid to the liquid state. In Embodiment 16, vacuum-vapor deposition was carried out under the same conditions as in Embodiment 13, while exposing the furylfulgide on the heating boat to UV light in this liquid state. By exposing the sample material on the heating boat directly to light in this way it was also possible to obtain the transparent glassy amorphous thin film of furylfulgide obtained in Embodiment 13.

[Benefits of the invention]

As described above, by using the method of the present invention for forming an amorphous organic film it becomes possible to form glassy amorphous films from compounds which do not readily give amorphous thin films by prior methods. Therefore, it enables vapor deposition of compounds with which vacuum deposition has hitherto been impossible, and enables dry formation of thin films from organic materials which currently only give thin films by wet methods. Use of the present method can be expected to offer considerable benefits for dry thin film formation of resists and other materials.

In addition, due to exposure to light, the organic material is formed into a thin film while in the excited state, and as a result they have functions not manifested by thin films formed by prior methods, opening up possible applications such as organic solar cells, for example.

Moreover, as indicated in the embodiments, NBPS films and furylfulgide films and also NDASB films and azobenzene films, which crystallize and cloud and form opaque thin films with prior methods, become amorphous with the present invention, and in the transparent amorphous state undergo reversible changes on exposure to UV or visible light (or heat), showing a *cis/trans* isomeric change or photochromism with a change between colored and colorless, and therefore can be used as writeable optical disk media; and because they give

simple thin films without the need to use a polymeric dispersant, high S/N ratios can be obtained.

4. Simplified description of the drawings

Fig. 1, Fig. 5, Fig. 6 and Fig. 7 are schematic cross-sectional drawings illustrating examples of a device for forming an amorphous organic film employed in the present invention. Fig. 2-1 is a spectral diagram measuring the roughness of an NBPS vacuum-vapor deposition film formed by a prior method; Fig. 2-2 is a spectral diagram determining the roughness of an amorphous NBPS vacuum-vapor deposition film formed by the present invention; Fig. 3 is the absorption spectra of the NBPS vacuum-vapor deposition films; Fig. 4-1 is the infrared absorption (IR) spectrum of the NBPS vacuum-vapor deposition film formed by the prior method; Fig. 4-2 is the infrared absorption (IR) spectrum of the amorphous NBPS vapor deposition film formed by the present invention; Fig. 8, Fig. 9 and Fig. 10 are absorption spectra of vacuum-vapor deposition thin films of the present invention.

11 : bell jar; 12 and 64 : substrate; 13 : UV light beam; 14, 51, 61 and 71 : 500 W ultrahigh-pressure mercury lamp; 15 : slit; 16, 55, 65 and 75 : sample material; 17, 56, 66 and 76 : heating boat; 18, 57, 67 and 77 : heating temperature control device; 19 : quartz glass window; 52 and 62 : reflecting mirror; 53, 63 and 73 : glass bell jar; 54 and 74 : quartz glass substrate;

58, 68 and 78 : light beam; 20, 59, 69 and 79 : colored filter.

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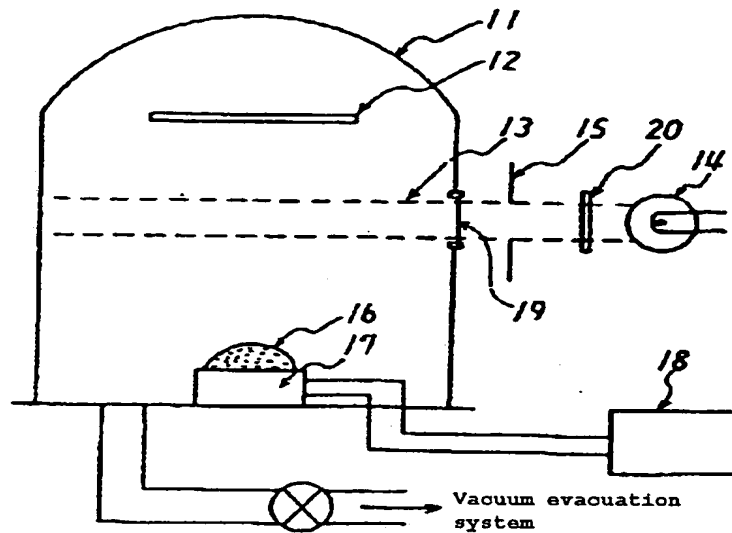


Figure 1

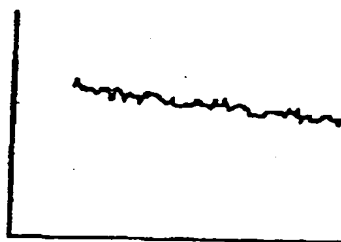


Figure 2.1

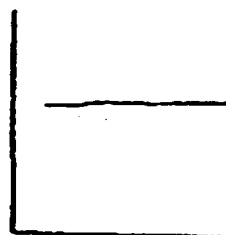


Figure 2.2

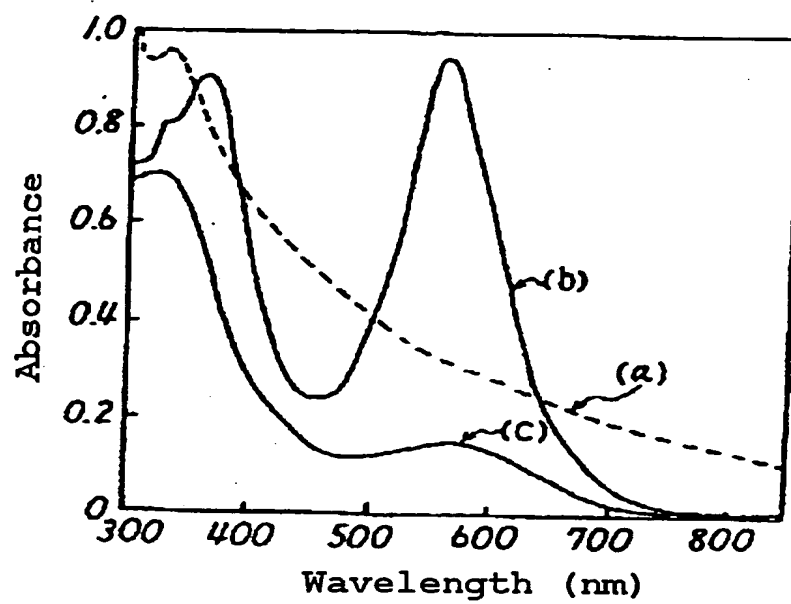


Figure 3

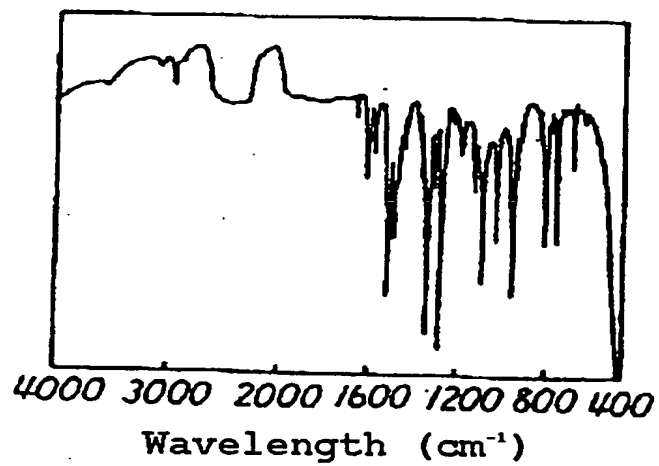


Figure 4.1

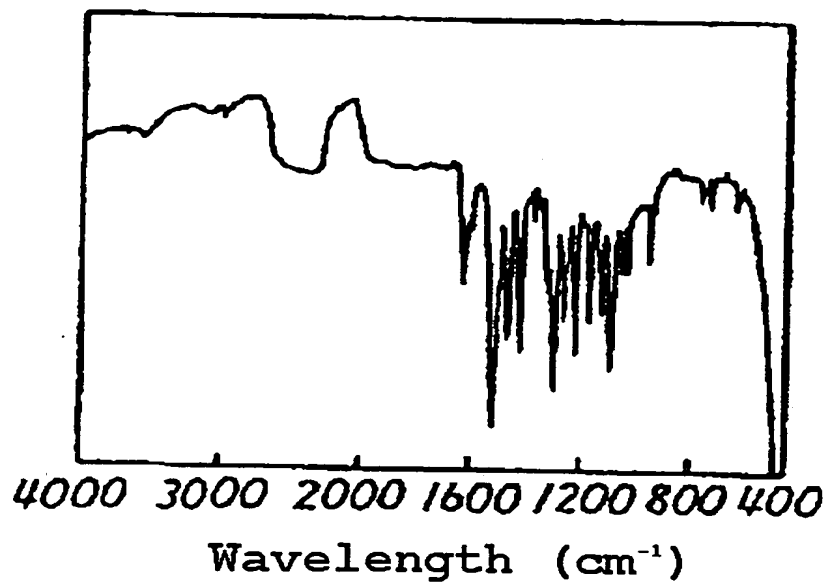


Figure 4.2

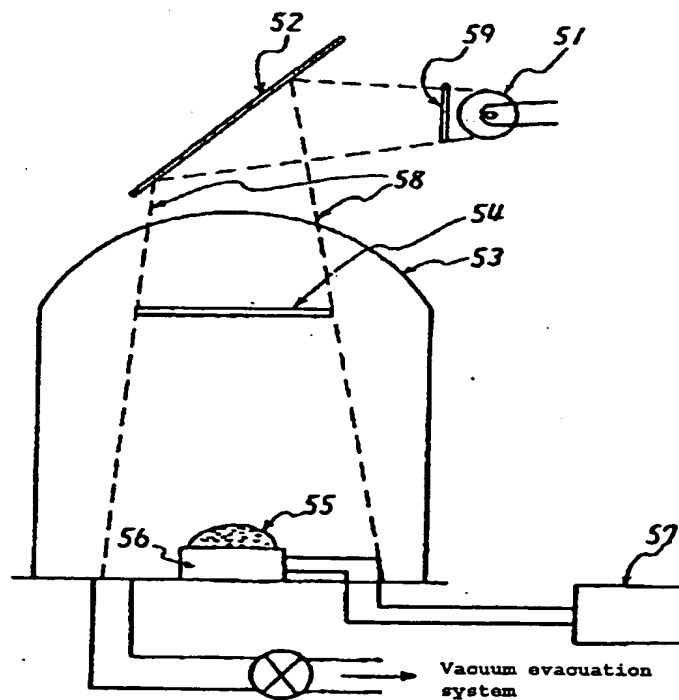


Figure 5

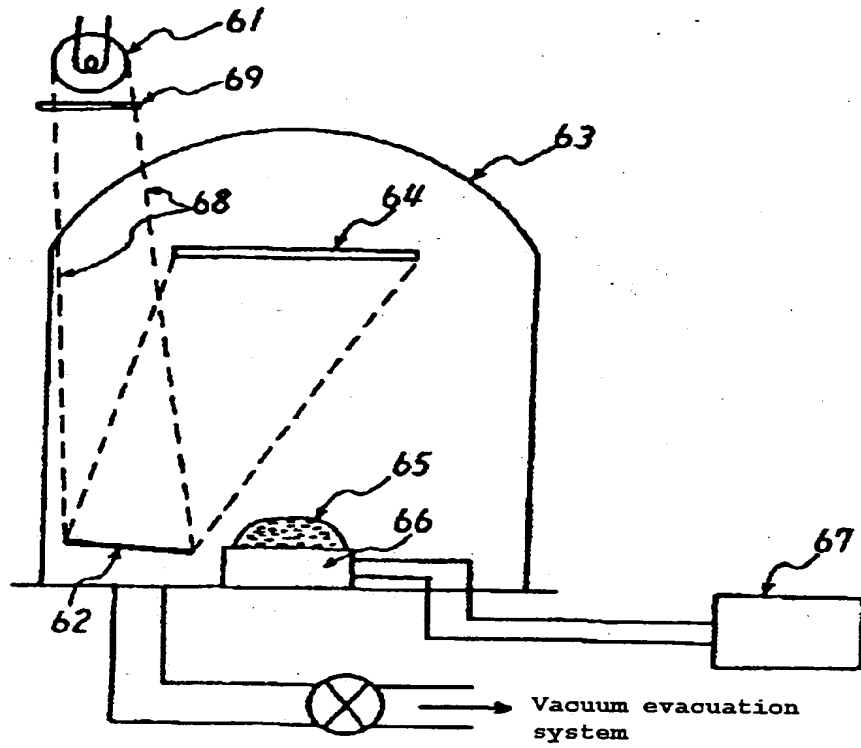


Figure 6

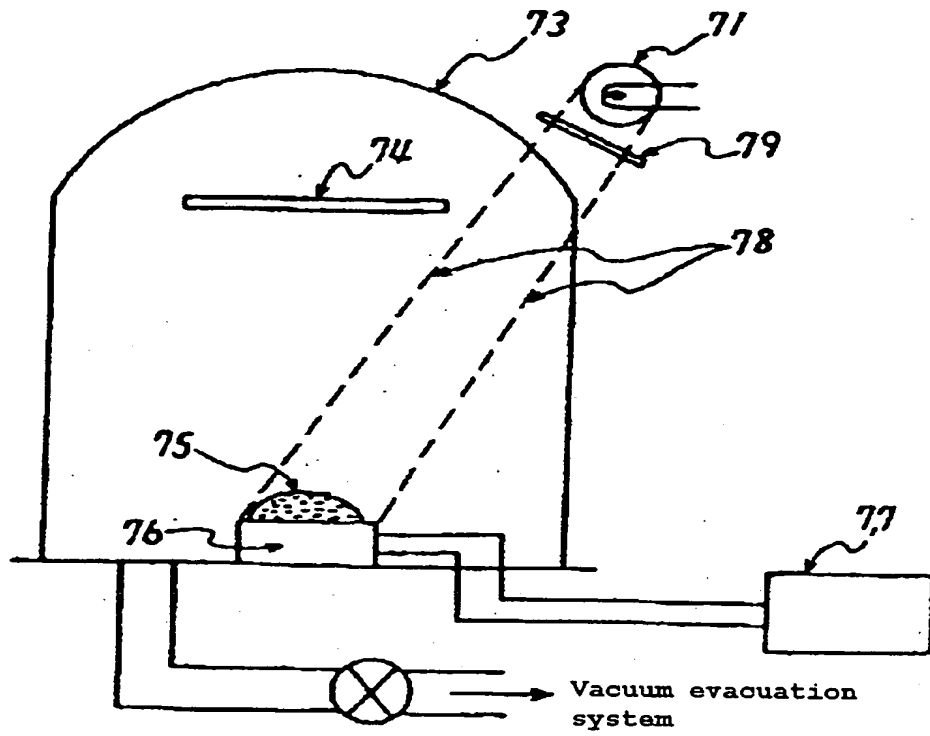


Figure 7

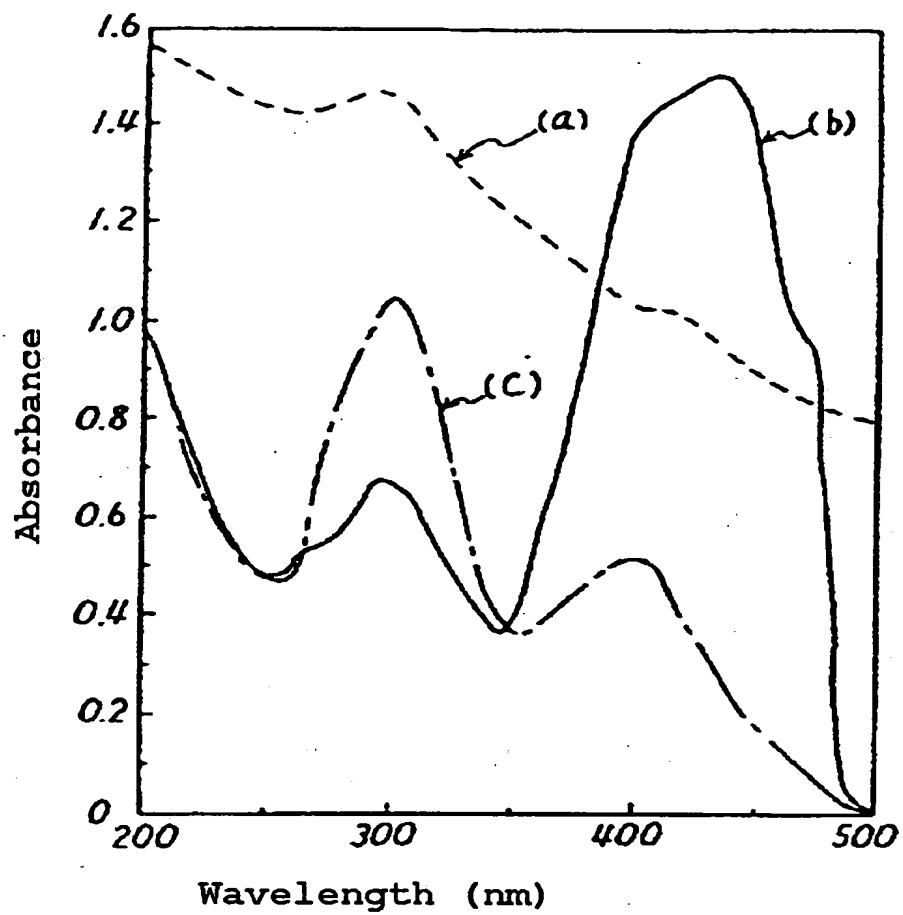


Figure 8

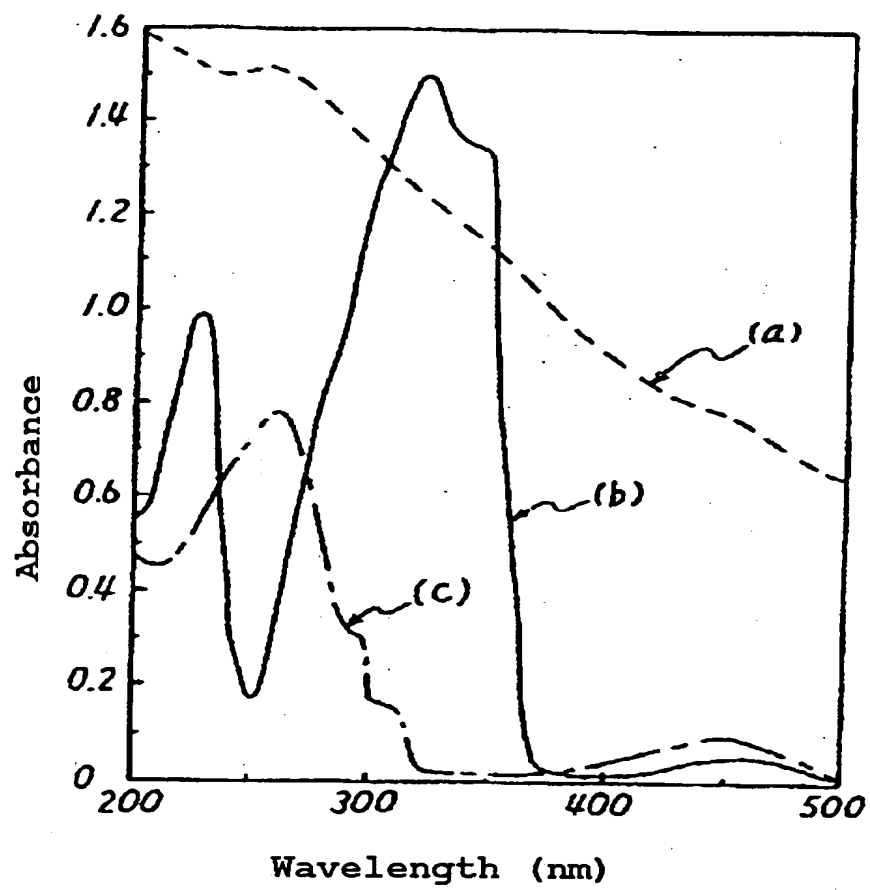


Figure 9

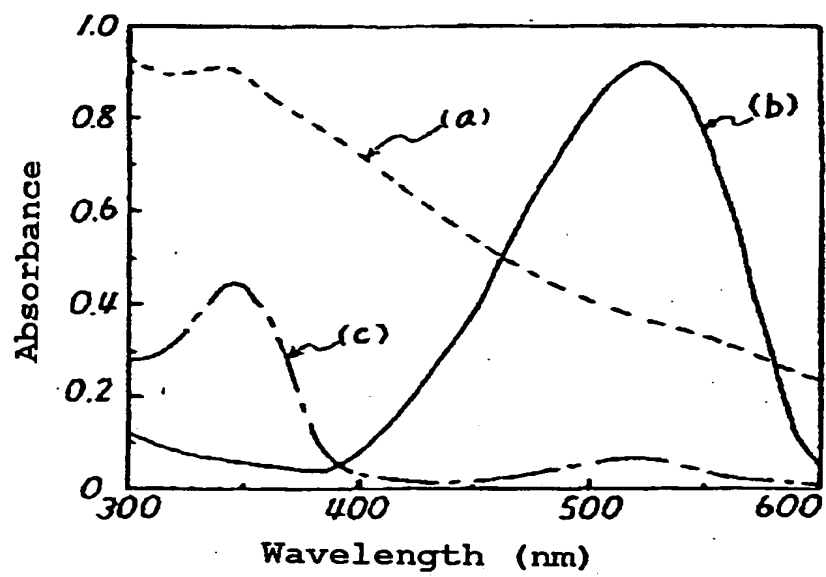


Figure 10